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(54) Granular adjuncts containing soil release polymers, and particulate detergent compositions containing th m

(57) A granular adjunct, for use in a particulate detergent composition of high bulk density, comprises a soil release polymer and an inorganic carrier material. The soil release polymer is preferably a graft copolymer of of vinyl acetate (optionally partially hydrolysed) on a backbone of polyethylene, polypropylene or polybutylene oxide. The preferred inorganic carrier material is sodium carbonate and/or sodium bicarbonate and/or sodium sesquicarbonate, optionally plus zeolite in a ratio of zeolite to carbonate salt within the range of from 1:1 to 3:1.

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GRANULAR ADJUNCTS CONTAINING SOIL RELEASE POLYMERS, AND PARTICULATE DETERGENT COMPOSITIONS CONTAINING THEM

TECHNICAL AREA

The present invention relates to a granular adjunct containing a soil release polymer, for example, a graft copolymer of vinyl acetate units on a polyethylene oxide backbone, and the use of the adjunct in particulate detergent compositions of high bulk density having improved detergency performance.

BACKGROUND AND PRIOR ART

EP 219 048A (BASF) discloses the use of graft copolymers of polyalkylene oxide with vinyl acetate as greying inhibitors in the washing and post-wash treatment of synthetic textile fabrics. Detergent compositions containing these polymers are also disclosed in EP 358 474A, EP 358 473A and EP 358 472A (Unilever).

Other soil release polymers widely disclosed in the art are polyesters of terephthalic and other aromatic dicarboxylic acids, in particular, the so-called PET/POET (polyethylene terephthalate/polyoxyethylene terephthalate) and PET/PEG (polyethylene terephthalate/polyethylene glycol) polymers which are disclosed, for example, in US 3 557 039 (ICI), GB 1 467 098 and EP 1305A (Procter & Gamble). Other patent publications disclosing soil release polymers include EP 185 427A, EP 241 984A, EP 241 985A, EP 272 033A and EP 357 280A (Procter & Gamble), and EP 442 101B (BASF).

Formulators of detergent powders conventionally make a distinction between the base powder and post-dosed (admixed, post-added) ingredients. The base powder contains most or all of the detergent-active compounds (surfactants) and detergency builders present, and the term indicates a substantially homogeneous material composed of substantially uniform identically composed granules.

In traditional powders of low or medium bulk density the base powder is generally prepared by spray-drying an aqueous slurry of the ingredients. In the compact powders of high bulk density that are currently favoured, the base powder may be prepared by mixing and granulation in a high-speed mixer/granulator. Other granulation and drying processes are well known to the detergents formulator.

Normally any ingredients that are sufficiently robust and stable to processing at elevated temperatures are included in the base powder together with the surfactants and builders. Such ingredients include soap, fluorescers, cellulosic antiredeposition agents, sodium silicate, sodium carbonate, acrylic or acrylic/maleic polymers, and soil release polymers. Ingredients that are sensitive to moisture or to elevated temperatures are postdosed to the base powder and, if particulate, remain as separate, discrete particles in the final product. Peroxy bleach compounds such as persalts and peroxyacids, bleach activators, enzymes, foam control compounds and perfumes are normally postdosed. Salts such as sodium carbonate, sodium sulphate and sodium citrate are sometimes postdosed rather than, or as well as, incorporated in the base powder.

The normal method for incorporating soil release polymers in detergent powders has been to include them in the base powder: for example, an aqueous polymer solution

may be included when preparing a slurry for spray-drying, or may be introduced directly into a high-speed mixer/granulator. However, it has been found that when this method of incorporation is used for powders of high bulk density, insoluble residues on washed articles are obtained.

The present invention is based on the discovery that, in powders of high bulk density, in particular those based on alkali metal aluminosilicate (zeolite) builder, soil release polymers may be most effectively incorporated as a postdosed granular adjunct in which the polymer is combined with an inorganic carrier material. Adjunct carrier materials having an optimum balance of liquid carrying capacity and dissolution rate have been identified. Polymers incorporated in this way are delivered rapidly to the wash and residues have not been encountered.

EP 421 664A (Rohm and Haas) discloses a granulate having a bulk density of at least 700 g/litre useful in detergent formulations, which granulate contains at least 10 wt% of polymer useful in such formulations and at least 20 wt% of at least one inorganic component which is also useful in such formulations. The polymers are preferably acrylic and acrylic/maleic copolymers and the preferred inorganic component is sodium sulphate.

EP 571 436B (Henkel) discloses a granular additive for detergents comprising 40-75 wt% of a homopolymeric or copolymeric (meth)acrylic acid sodium salt, 1-35 wt% of hydrated zeolite, 2-20 wt% sodium sulphate, and 1-15 wt% water.

Gran[illegible] additives containing lower levels of polymers are [illegible] art. In these materials the polymer functions primarily as a bind[illegible]

compositions intended as carriers for mobile nonionic surfactants, or as builder or water-softener additives. For example, EP 184 794B and US 4 707 290 (Henkel) disclose an absorptive solid carrier material for use in detergent compositions, comprising 60-80 wt% of zeolite A or X, 0.1-5 wt% of sodium silicate, 3-15 wt% of acrylic or acrylic/maleic copolymer, optionally up to 5 wt% of ethoxylated nonionic surfactant, and 8-18 wt% of water removable at 130°C. Further disclosures of absorptive carrier granules containing zeolite and acrylic polymers include EP 344 629A, EP 424 403A, EP 425 804A and WO 92 10559A (Henkel), and EP 289 767A and EP 289 768A (Degussa).

EP 243 908A (Henkel) discloses a granular phosphate-free water softener additive for detergent compositions comprising 50-60 wt% of zeolite [illegible]e crystallin[illegible] wt% of acrylic or acrylic/maleic [illegible] w[illegible] [illegible]dium citrate, 4-12 wt% of sod[illegible] up to 2 wt% of sodium carbo[illegible]ellulose, and 12-25 wt% of water. WO 92 07928A (Henkel) discloses a granular builder composition comprising zeolite (60-96 wt%), acrylic or acrylic/maleic polymer (2-16 wt%), layered silicate (2-25 wt%), and optionally low levels of phosphonate sequestrant.

GB 2 164 048B (Colgate-Palmolive) discloses detergent compositions containing discrete granules prepared by comelting a PET/POET soil release polymer with polyacrylate, and converting the melt to solid particulate form (eg flakes or grinds). GB 2 169 917A (Colgate-Palmolive) discloses similar granules which are comelts of soil release polymer with any antiredeposition polymer.

DEFINITION OF THE INVENTION

A first subject of the present invention is a granular adjunct for use in a particulate detergent composition having a bulk density of at least 600 g/litre, which adjunct comprises a soil release polymer and an inorganic carrier material.

A second subject of the present invention is a process for the preparation of a granular adjunct as defined in the previous paragraph, which process includes the step of mixing and granulating an inorganic carrier material with a soil release polymer in a high-speed mixer/granulator.

A third subject of the present invention is a particulate detergent composition having a bulk density of at least 600 g/litre, comprising:

(i) from 40 to 90 wt% of a non-spray-dried homogeneous particulate base powder having a bulk density of at least 600 g/litre, comprising from 5 to 50 wt% of one or more detergent-active compounds and from 10 to 80 wt% of a detergency builder,

(ii) from 1 to 15 wt% of separate granules comprising a soil release polymer and an inorganic carrier material, and optionally

(iii) other ingredients in the form of separate particles or granules, to 100 wt%.

DETAILED DESCRIPTION OF THE INVENTION

The granular adjunct

The adjunct of the present invention contains two essential ingredients: a soil release polymer, and an inorganic carrier material. Various optional ingredients may also be present.

The soil release polymer

A preferred soil release polymer for use in the granular adjunct and detergent compositions of the present invention is a graft copolymer in which polyvinyl acetate and/or hydrolysed polyvinyl acetate (polyvinyl alcohol) groups are grafted onto a polyalkylene oxide (preferably polyethylene oxide) backbone.

Polymers of this type are described and claimed in EP 219 048A (BASF). These polymers are obtainable by grafting a polyalkylene oxide of molecular weight (number average) 2000 - 100 000 with vinyl acetate, which may be hydrolysed to an extent of up to 15%, in a weight ratio of polyalkylene oxide to vinyl acetate of 1:0.2 to 1:10. The polyalkylene oxide may contain units of ethylene oxide, propylene oxide and/or butylene oxide; polyethylene oxide is preferred.

Preferably the polyalkylene oxide has a number-average molecular weight of from 4000 to 50 000, and the weight ratio of polyalkylene oxide to vinyl acetate is from 1:0.5 to 1:6. Especially preferred are polymers derived from polyethylene oxide of molecular weight 2000-50 000 and having a weight ratio of polyethylene oxide to vinyl acetate of from 1:0.5 to 1:6.

A material within this definition, based on polyethylene oxide of molecular weight 6000 (equivalent to 136 ethylene oxide units), containing approximately 3 parts by weight of vinyl acetate units per 1 part by weight of polyethylene oxide, and having itself a molecular weight of 24 000, is commercially available from BASF as Sokalan (Trade Mark) HP22 and HP23.

Other soil release polymers for use in the present invention include the PET/POET polymers disclosed in US 3 557 039 (ICI), GB 1 467 098 and EP 1305A (Procter & Gamble). Polymers of this type are available commercially, for example, as Permalose, Aquaperle and Milease (Trade Marks) (ICI) and Repel-O-Tex (Trade Mark) SRP3 (Rhône-Poulenc).

The soil release polymer preferably constitutes from 5 to 30 wt%, more preferably from 15 to 25 wt%, of the granular adjunct of the invention.

The inorganic carrier material

The inorganic carrier material, which preferably constitutes from 50 to 75 wt% of the granular adjunct of the invention, is chosen to provide the best combination of carrying capacity and dissolution characteristics.

Preferred [illegible] carriers for use in the granular adjunct of the invention [illegible] and/or sodium bicarbonate and/or sodium [illegible] optionally in combination with zeolite.

A first preferred embodiment of the invention is an adjunct which may be prepared by a non-spray-drying process (described in more detail below), in which the carrier is

sodium carbonate, sodium bicarbonate or a mixture of the two, in combination with zeolite.

In this embodiment, the zeolite suitably constitutes from 35 to 60 wt% of the granular adjunct, while the carbonate-based salt suitably constitutes from 15 to 30 wt%. The ratio of zeolite to carbonate-based salt may vary, for example, from 0.5:1 to 9:1, and for the optimum balance between carrying capacity and dissolution is preferably from 1:1 to 3:1.

Zeolites are crystalline alkali metal aluminosilicates having the general formula:

$$0.8\text{-}1.5\ Na_2O.\ Al_2O_3.\ 0.8\text{-}6\ SiO_2$$

These materials also contain some bound water. Preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above).

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, advantageously, the zeolite present in the adjuncts of the invention may be maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably not exceeding 1.15, more preerably not exceeding 1.07, most preferably about 1.00.

A second preferred embodiment of the invention is an adjunct in which the carrier may be prepared by spray-drying and subsequent densification (described in more detail below). The preferred carrier material in this embodiment is sodium carbonate and/or sodium

sesquicarbonate. In this embodiment, the sodium carbonate-based carrier material may generally constitute from 50 to 75 wt% of the granular adjunct.

Optional ingredients

Advantageously, the granular adjunct of the invention may also contain a significant amount of another detergent-functional polymer, notably a polycarboxylate polymer. In this way a single granular adjunct may be used to deliver two different functional polymers.

Preferred polycarboxylate polymers are efficient binders of calcium ions, preferably having a $pK_{Ca}2+$ of at least 5.5, as measured with a calcium-sensitive electrode, for example, as described by M Floor et al, Carbohydrate Research 203 (1990) pages 19 to 32.

The polycarboxylate polymers are preferably polymers of unsaturated monocarboxylic acids and/or unsaturated dicarboxylic acids. Suitable monocarboxylic monomers include acrylic, methacrylic, vinylacetic, and crotonic acids, most preferably acrylic acid; suitable dicarboxylic monomers include maleic, fumaric, itaconic, mesaconic and citraconic acids, most preferably maleic acid, and their anhydrides. The polymers may also contain units derived from non-carboxylic monomers, for example, olefins or methyl vinyl ether, preferably in minor amounts. The polymers may be in acid, salt or partially neutralised form.

Especially preferred are copolymers of acrylic and maleic acids, for example, Sokalan (Trade Mark) CP5 (salt form) and CP45 (partially neutralised form) (70% acrylic, 50% maleic) and CP7 (50% acrylic, 50% maleic).

Other suitable polymers are homopolymers of acrylic acid, for example, Sokalan (Trade Mark) PA40; polymers of maleic acid with methyl vinyl ether, for example, Sokalan (Trade Mark) CP2; and polymers of acrylic acid with olefin, for example, Sokalan (Trade Mark) CP9.

Polycarboxylate polymers may suitably be present in the adjunct in amounts of up to 30 wt%, preferably from 15 to 25 wt%. When polycarboxylate polymer is present, the amount of soil release polymer in the adjunct will generally be lower, for example, 5 to 10 wt%.

Ethoxylated nonionic surfactants may also be present if desired. These may be introduced via the soil release polymer if available as a liquid premix containing ethoxylated nonionic surfactant; for example, Sokalan HP23 mentioned above is a mixture of 60 wt% polymer and 40 wt% ethoxylated nonionic surfactant (Lutensol (Trade Mark) A7N). Ethoxylated nonionic surfactant is suitably present in an amount of up to 20 wt%, preferably from 2 to 15 wt%.

Preferred adjunct compositions

The adjunct in accordance with the invention suitably has the following general composition:

(a) from 5 to 30 wt% of soil release polymer,
(b) from 0 to 30 wt% of acrylic polymer,
(c) from 0 to 20 wt% of ethoxylated nonionic surfactant,
(d) from 10 to 75 wt% of sodium carbonate and/or sodium bicarbonate and/or sodium sesquicarbonate,
(e) from 0 to 60 wt% of zeolite,
(f) water to 100 wt%.

The first preferred embodiment of the invention comprises:

(a) from 5 to 30 wt% of soil release polymer,
(c) from 10 to 15 wt% of ethoxylated nonionic surfactant,
(d) from 15 to 30 wt% of sodium carbonate and/or sodium bicarbonate,
(e) from 35 to 60 wt% of zeolite,
(f) water to 100 wt%.

The second preferred embodiment of the invention comprises:

(a) from 5 to 30 wt% of soil release polymer,
(b) from 15 to 25 wt% of acrylic polymer,
(c) from 2 to 15 wt% of ethoxylated nonionic surfactant,
(d) from 50 to 75 wt% of sodium carbonate and/or sodium sesquicarbonate,
(f) water to 100 wt%.

Thus the inclusion of polycarboxylate polymer is especially appropriate to the second preferred embodiment of the invention.

Particle size and bulk density

The adjunct granules of the invention preferably have an average particle size of at least 300 μm and preferably at least 400 μm. Most preferably the adjunct granules have an average particle size within the range of from 400 to 800 μm.

The adjunct granules of the invention preferably have a bulk density of at least 400 g/litre and more preferably at least 500 g/litre.

Preparation of the granular adjunct

The granular adjuncts of the invention are of high bulk density and are preferably prepared by a process route which involves the use of a high-speed mixer/granulator having both a stirring and a cutting action to mix and granulate the soil release polymer (generally in solution or suspension form) and the inorganic carrier material.

The high-speed mixer/granulator, also known as a high-speed mixer/densifier, may be a batch machine such as the Fukae (Trade Mark) FS, or a continuous machine such as the Lödige (Trade Mark) Recycler CB30. Suitable machines and processes are described, for example, in EP 340 013A, EP 367 339A, EP 390 251A, EP 420 317A, EP 506 184A and EP 544 492A (Unilever).

As previously indicated, two preferred processes are contemplated.

In a first process, appropriate for the first preferred embodiment of the invention, the raw materials - the inorganic carrier material, the soil release polymer and any optional ingredients - are mixed and granulated directly in the high-speed mixer/granulator.

For the first preferred embodiment of the invention, therefore, the process comprises mixing and granulating sodium carbonate and/or sodium bicarbonate, zeolite and a solution or suspension of the soil release polymer, in a high-speed mixer/granulator. The process produces adjuncts having a bulk density of at least 600 g/litre.

The adjuncts may be finished by further processing, for example, in a moderate-speed mixer/granulator such as the Lödige Ploughshare. If desired, part of the zeolite may be withheld from the initial processing and added at this stage to form an outer layer which will facilitate handling. The adjunct granules may then be dried and cooled in a fluidised bed.

In a second preferred process, appropriate for the second preferred embodiment of the invention, a porous inorganic carrier material of low bulk density is prepared by spray-drying an aqueous slurry, and this is then granulated and densified with the soil release polymer in the high-speed mixer/granulator. Thus the second preferred process of the invention comprises:

(i) spray-drying an aqueous slurry comprising an inorganic carrier material to form a granular spray-dried carrier material,

(ii) mixing and granulating the spray-dried carrier material prepared in step (i) with a solution or suspension of the soil release polymer, in a high-speed mixer/granulator.

As indicated, this process is preferred for the preparation of adjuncts of the second preferred embodiment of the invention, that is to say, adjuncts utilising a wholly sodium carbonate-based carrier material, and is especially suitable for adjuncts containing a polycarboxylate polymer. The polycarboxylate polymer included in the spray-dried carrier material will effect some crystal growth modification and improve the carrying capacity of the sodium carbonate-based carrier.

For this type of adjunct the process steps comprise:

(i) spray-drying an aqueous slurry comprising sodium carbonate and/or sodium sesquicarbonate and acrylic polymer to form a granular spray-dried carrier material,

(ii) mixing and granulating the spray-dried carrier material prepared in step (i) with further sodium carbonate and with a solution or suspension of the soil release polymer, in a high-speed mixer/granulator.

This process produces adjuncts having a bulk density of at least 500 g/litre.

In both processes, the soil release polymer may be incorporated in aqueous solution form. For example, Sokalan HP22 mentioned above is available as a 20 wt% aqueous solution. Advantageously, however, a liquid premix of soil release polymer and ethoxylated nonionic surfactant, such as the Sokalan HP23 premix (60 wt% polymer, 40 wt% surfactant), is used. This, because of its higher polymer content, allows the preparation of an adjunct having a higher polymer content than is possible using the aqueous solution.

In principle, premixes containing higher levels of polymer may be used provided that the viscosity is not so high that processing becomes difficult.

Detergent compositions

The granular adjuncts of the present invention may be utilised in particulate detergent compositions of high bulk density, that is to say, at least 600 g/litre, preferably at least 650 g/litre, and more preferably at least 700 g/litre. The detergent compositions of the invention are composed of at least two different discrete granules: the base powder, and the postdosed polymer/carrier adjunct granules. Further postdosed particulate materials may also be present, for example, peroxy bleach compounds.

The granules may suitably be present in the detergent composition in an amount of from 1 to 20 wt%, preferably from 2 to 15 wt%. Granules containing both soil release polymer and polycarboxylate polymer will generally be used at higher levels, for example, 7 to 15 wt%, than will granules containing only soil release polymer, where lower levels, for example, from 2 to 10 wt% may be preferred.

The detergent base powder

The detergent base powder contains, as essential ingredients, detergent-active compounds (surfactants) and detergency builders.

The detergent-active compounds may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkylsulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

The preferred surfactant system for the compositions of the invention comprises one or more anionic sulphonate or sulphate type surfactants, in combination with one or more nonionic surfactants, optionally in conjunction with a minor amount of soap. Especially preferred surfactant systems comprise alkylbenzene sulphonate and/or primary alcohol sulphate in combination with ethoxylated alcohol nonionic surfactant.

The total amount of surfactant present ranges from 5 to 50 wt% (based on the whole product including postdosed ingredients), preferably from 10 to 30 wt% and more preferably from 15 to 25 wt%.

The base powder also contain one or more detergency builders. The total amount of detergency builder in the compositions will suitably range from 10 to 90 wt%, preferably from 10 to 60 wt%.

The builder system preferably consists wholly or partially of an alkali metal aluminosilicate. This is suitably present in an amount of from 10 to 90 wt% (based on the anhydrous material), preferably from 10 to 60% by weight and more preferably from 25 to 50 wt%.

The preferred alkali metal aluminosilicates are described above in the context of the adjunct granules. The zeolites preferably used, as in the adjuncts, are zeolite A or zeolite MAP, as described above.

Supplementary builders may also be present in the base powder. Polycarboxylate polymers may be present in the base powder whether or not they are also postdosed. other organic supplementary builders include monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts.

Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

The compositions of the invention may contain alkali metal, preferably sodium, carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%, and may be incorporated in the base powder, postdosed as separate particles or granules, or both, as well as present (preferably) in the adjunct granules of the invention.

The base powder may incorporate a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, or sodium silicate. As previously indicated, polycarboxylate polymers may also be present in the base powder, in addition to any polymer present as postdosed particles or granules, in order to aid structuring. One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%.

Other ingredients that may be present in the detergent base powder include fluorescers, inorganic salts, cellulosic antiredeposition agents, and water.

Postdosed ingredients

As well as the adjunct granules of the invention, additional postdosed ingredients may be present.

The compositions may, for example, contain a peroxy bleach compound, for example, an inorganic persalt or organic peroxyacid. Preferred inorganic persalts include sodium perborate monohydrate and tetrahydrate, and sodium percarbonate. The peroxy bleach compound is suitably present in an amount of from 5 to 35 wt%, preferably from 10 to 25 wt%.

The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%. Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxycarbonic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED).

A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as ethylenediamine tetramethylene phosphonate (EDTMP) or diethylenetriamine pentamethylene phosphonate (DETPMP).

An especially preferred bleach system comprises a peroxy bleach compound, preferably sodium percarbonate, together with a bleach activator, preferably TAED, and a polyphosphonate bleach stabiliser.

Other materials that may be present as postdosed ingredients in detergent compositions of the invention include sodium silicate; fluorescers; inorganic salts such as sodium sulphate; foam control agents; enzymes; dyes; coloured speckles; perfumes; and fabric softeners.

Preparation of the detergent compositions

The particulate detergent compositions of the invention are of high bulk density and, as previously indicated, are composed of a homogeneous particulate base powder, and postdosed ingredients.

The base powder may be prepared by any method that yields substantially homogeneous granules of high bulk density. As in the preparation of the adjuncts of the invention, this may be achieved by post-tower densification of a spray-dried powder, or, in this case preferably, by a wholly non-tower (non-spray-drying) process in which liquid and solid ingredients are mixed and granulated together. In both cases a high-speed mixer/granulator, as described above, may advantageously be used. The further processing steps described above, for example, using a moderate-speed mixer/granulator and a fluidised bed, may be also be carried out as appropriate.

Liquid ingredients unsuitable for incorporation in the base powder, for example, mobile ethoxylated nonionic surfactants and perfume may be sprayed on or otherwise mixed into the base powder, and the adjunct granules, bleach ingredients (bleaches, bleach precursor, bleach stabilisers), proteolytic and lipolytic enzymes, coloured speckles, perfumes, foam control granules and any other granular or particulate ingredients not included in the base powder incorporated by dry mixing.

EXAMPLES

The invention will be further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise indicated.

EXAMPLES 1 TO 4: GRANULAR ADJUNCTS

Examples 1 to 3

Adjuncts according to the first preferred embodiment of the invention were prepared to the following formulations (in weight %):

	1	2	3
Sodium carbonate	-	10.5	20.7
Sodium bicarbonate	21.5	10.5	-
Zeolite MAP* (in granule)	38.7	44.7	44.0
(layered)	8.6	4.2	4.1
Soil release polymer**	18.7	18.0	18.7
Nonionic 7EO**	12.5	12.0	12.5

*as described and claimed in EP 384 070A (Unilever): Doucil (Trade Mark) A24 ex Crosfield Chemicals.

**Graft polyvinyl acetate/polyethylene oxide copolymer, Sokalan HP23 ex BASF, supplied as premix with the nonionic surfactant.

The adjuncts were prepared as follows. The salt (carbonate, bicarbonate or mixture) was granulated with the major part of the zeolite MAP and the polymer/nonionic surfactant blend in a Lödige Recycler continuous high-speed mixer/granulator heated to 70°C and operated at 1200-1500 rpm. From the Recycler the granulate passed to a Lödige Ploughshare moderate-speed mixer/granulator, operated at 120 rpm with low residence time and choppers on, where the remaining zeolite was added for layering. The granules then passed to a fluidised bed for cooling and elutriation of fine particles.

Throughputs in kg/h were as follows:

	1	2	3
Sodium carbonate	-	100	200
Sodium bicarbonate	200	100	-
Zeolite MAP (in granule)	360	425	425
(layered)	80	40	40
Polymer/nonionic	290	285	300

Physical properties were as follows:

	1	2	3
Bulk density (g/litre)			
ex Ploughshare	770-800	785	
ex fluidised bed	740-810		790
Dynamic flow rate (ml/s)			
ex Ploughshare	85-115	70	
ex fluidised bed	135-145		145

The average particle size dp was 540-650 μm for all three Examples.

Example 4

An adjunct according to the second preferred embodiment of the invention was prepared to the following formulation (in weight %):

Sodium sesquicarbonate	30.8
Sodium carbonate	27.0
Acrylic/maleic copolymer*	19.1
Soil release polymer**	7.4
Nonionic surfactant 7EO**	4.9
Water	10.8

*Sokalan CP5 ex BASF (sodium salt form of polymer)
**Sokalan HP23 premix as used in Examples 1 to 3

An aqueous slurry was prepared by mixing 100 parts of sodium carbonate vigorously into 100 parts of water to form a supersaturated solution, then mixing in 100 parts of Sokalan CP45 (the acid form of Sokalan CP5, 45 wt% aqueous solution) to effect reaction with the carbonate to form sesquicarbonate and the sodium salt Sokalan CP5. The slurry was spray-dried to form a free-flowing powder having a moisture content which could be varied from 2 to 18 wt%. The bulk density was 380-470 g/litre, dynamic flow rate was 90-125 ml/s, and particle size dp was 280-340 μm.

Spray-dried powder having a moisture content of 14-18 wt% was granulated in the Lödige Recycler continuous high-speed mixer/granulator with Sokalan HP23 soil release polymer/nonionic surfactant premix (as used in Examples 1 to 3) and further sodium carbonate, to form a granular product of the composition above, having a bulk density of 525-600 g/litre and a dynamic flow rate of 75-115 ml/s. This product had an especially fast dissolution rate (95 wt% dissolved in demineralised water in <1 min).

EXAMPLES 5 to 8: DETERGENT COMPOSITIONS

Detergent powders of high bulk density were prepared to the formulations shown below. The base powder (the same for all) was prepared by mixing and granulation in a Lödige Recycler high-speed mixer/granulator, and the remaining ingredients were postdosed.

Examples 5 and 6: bleaching formulations

	5	6
Na primary alcohol sulphate	11.76	11.67
Nonionic surfactants	5.87	5.83
Na soap	1.84	1.83
Zeolite MAP (anhydrous basis)	22.74	22.57
Sodium citrate	3.31	3.29
Sodium carbonate	2.33	2.32
Sodium carboxymethylcellulose	0.91	0.90
Minor ingredients and water	5.03	4.99
Total base powder	53.80	53.40
Sodium percarbonate	19.00	19.00
TAED* (83% active)	5.50	5.50
EDTMP** (34% active)	0.42	0.42
Antifoam granule	3.78	3.78
Sodium carbonate	8.20	6.65
Sodium bicarbonate	1.00	1.00
Acrylic/maleic copolymer***	1.80	-
Polymer adjunct (Example 3)	4.50	-
Polymer adjunct (Example 4)	-	8.25
Enzymes	1.55	1.55
Perfume	0.45	0.45
Total	100.00	100.00

Examples 7 and 8: non-bleaching formulations

	7	8
Na primary alcohol sulphate	12.00	12.00
Nonionic surfactants	6.00	6.00
Na soap	1.79	1.79
Zeolite MAP (anhydrous basis)	23.94	23.94
Sodium citrate	3.52	3.52
Sodium carbonate	2.38	2.38
Sodium carboxymethylcellulose	0.72	0.72
Minor ingredients and water	5.10	5.10
Total base powder	55.45	55.45
Antifoam/PVP granule	4.00	4.00
Sodium carbonate	18.38	16.74
Sodium bicarbonate	8.00	6.50
Acrylic/maleic copolymer***	3.00	-
Polymer adjunct (Example 3)	7.50	-
Polymer adjunct (Example 4)	-	13.64
EDTMP**	1.40	1.40
Enzymes	1.83	1.83
Perfume	0.45	0.45
Total	100.00	100.00

*tetraacetylethylenediamine

**ethylenediamine tetramethylene phosphonate

***granular Sokalan CP5 or CP7

The bulk density of the base powder was 914 g/litre and the bulk densities of the final products were all above 850 g/litre.

All powders showed excellent detergency and no insoluble residues were found on the washed fabrics.

* * *

CLAIMS

1 A granular adjunct for use in a particulate detergent composition having a bulk density of at least 600 g/litre, which comprises a soil release polymer and an inorganic carrier material.

2 A granular adjunct as claimed in claim 1, wherein the soil release polymer is a graft copolymer of of vinyl acetate (optionally partially hydrolysed) on a backbone of polyethylene, polypropylene or polybutylene oxide.

3 A granular adjunct as claimed in claim 2, wherein the soil release polymer is a graft copolymer obtainable by grafting a polyalkylene oxide of molecular weight (number average) 2000 - 100 000 with vinyl acetate (optionally partially hydrolysed) in a weight ratio of polyalkylene oxide to vinyl acetate of 1:0.2 to 1:10.

4 A granular adjunct as claimed in claim 3, wherein the soil release polymer is a graft copolymer obtainable by grafting a polyethylene oxide of molecular weight (number average) 2000 - 50 000 with vinyl acetate (optionally partially hydrolysed) in a weight ratio of polyethylene oxide to vinyl acetate of 1:0.5 to 1:6.

5 A granular adjunct as claimed in any preceding claim, which comprises from 5 to 30 wt% of soil release polymer.

6 A granular adjunct as claimed in claim 5, which comprises from 15 to 25 wt% of soil release polymer.

7 A granular adjunct as claimed in any preceding claim, which comprises from 50 to 75 wt% of the inorganic carrier material.

8 A granular adjunct as claimed in any preceding claim, wherein the inorganic carrier material comprises sodium carbonate and/or sodium bicarbonate and/or sodium sesquicarbonate.

9 A granular adjunct as claimed in claim 8, wherein the inorganic carrier material further comprises zeolite.

10 A granular adjunct as claimed in claim 9, wherein the ratio of zeolite to carbonate salt is within the range of from 1:1 to 3:1.

11 A granular adjunct as claimed in any preceding claim, which further comprises an ethoxylated nonionic surfactant.

12 A granular adjunct as claimed in any preceding claim, which further comprises a polycarboxylate polymer.

13 A granular adjunct as claimed in claim 12, wherein the acrylic polymer is an acrylic/maleic copolymer.

14 A granular adjunct as claimed in any preceding claim, which comprises:

(a) from 5 to 30 wt% of soil release polymer,

(b) from 0 to 30 wt% of acrylic polymer,

(c) from 0 to 20 wt% of ethoxylated nonionic surfactant,

(d) from 10 to 75 wt% of sodium carbonate and/or sodium bicarbonate and/or sodium sesquicarbonate,

(e) from 0 to 60 wt% of zeolite, and

(f) water to 100 wt%.

15 A granular adjunct as claimed in claim 14, which comprises:

(a) from 5 to 30 wt% of soil release polymer,

(c) from 10 to 15 wt% of ethoxylated nonionic surfactant,

(d) from 15 to 30 wt% of sodium carbonate and/or sodium bicarbonate,

(e) from 35 to 60 wt% of zeolite, and

(f) water to 100 wt%.

16 A granular adjunct as claimed in claim 14, which comprises:

(a) from 5 to 30 wt% of soil release polymer,

(b) from 15 to 25 wt% of acrylic polymer,

(c) from 2 to 15 wt% of ethoxylated nonionic surfactant,

(d) from 50 to 75 wt% of sodium carbonate and/or sodium sesquicarbonate, and

(f) water to 100 wt%.

17 A granular adjunct as claimed in any preceding claim, which has an average particle size of at least 300 μm.

18 A granular adjunct as claimed in claim 17, which has an average particle size within the range of from 400 to 800 μm.

19 A granular adjunct as claimed in any preceding claim, which has a bulk density of at least 500 g/litre.

20 A granular adjunct substantially as hereinbefore described in any one of Examples 1 to 4.

21 A process for the preparation of a granular adjunct as claimed in claim 1, which process includes the step of mixing and granulating an inorganic carrier material with a soil release polymer, in a high-speed mixer/granulator.

22 A process as claimed in claim 21, which comprises mixing and granulating sodium carbonate and/or sodium bicarbonate, zeolite and a solution or suspension of the soil release polymer, in a high-speed mixer/granulator.

23 A process as claimed in claim 21, which comprises:

(i) spray-drying an aqueous slurry comprising an inorganic carrier material to form a granular spray-dried carrier material,

(ii) mixing and granulating the spray-dried carrier material prepared in step (i) with a solution or suspension of the soil release polymer, in a high-speed mixer/granulator.

24 A process as claimed in claim 23, which comprises:

(i) spray-drying an aqueous slurry comprising sodium carbonate and/or sodium sesquicarbonate and acrylic polymer to form a granular spray-dried carrier material,

(ii) mixing and granulating the spray-dried carrier material prepared in step (i) with further sodium carbonate and with a solution or suspension of the soil release polymer, in a high-speed mixer/granulator.

25 A process for the preparation of a granular adjunct carried out substantially as hereinbefore described in any one of Examples 1 to 4.

26 A particulate detergent composition having a bulk density of at least 600 g/litre, comprising:

(i) from 40 to 90 wt% of a non-spray-dried homogeneous particulate base powder having a bulk density of at least 600 g/litre, comprising from 5 to 50 wt% of one or more detergent-active compounds and from 10 to 80 wt% of a detergency builder,

(ii) from 1 to 20 wt% of separate adjunct granules comprising a soil release polymer and an inorganic carrier material, and optionally

(iii) other ingredients in the form of separate particles or granules, to 100 wt%.

27 A detergent composition as claimed in claim 26, which comprises from 2 to 15 wt% of the soil release polymer adjunct granules.

28 A detergent composiiton as claimed in claim 27, wherein the granules further comprise a polycarboxylate polymer and are present in an amount of from 7 to 15 wt%.

29 A detergent composition as claimed in claim 27, wherein the granules do not contain a polycarboxylate polymer and are present in an amount of from 2 to 10 wt%.

30 A detergent composition substantially as hereinbefore described in any one of Examples 5 to 8.

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Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report)	Application number GB 9518015.4
Relevant Technical Fields (i) UK Cl (Ed.O) C5D (DHC, DHZ) DJA (ii) Int Cl (Ed.6) C11D	Search Examiner M J CONLON Date of completion of Search 15 FEBRUARY 1996
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE: WPI	Documents considered relevant following a search in respect of Claims :- 1-30

Categories of documents

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A	EP 219328 A2 (UNILEVER)	1

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